

Optical Properties of Closely Coupled Dilute Nitride Mid-Infrared InNSb Quantum Dots

S. M. Kim^{1,2}, F. Hatami², H. Yuen², A. Chin³,
P. Kung¹ and J. S. Harris²

¹ Department of Electrical and Computer Engineering, The University of Alabama, Tuscaloosa, Alabama 35487, USA

² Solid State and Photonics Laboratory, Department of Electrical Engineering, Stanford University, Stanford, California, 94305, USA

³ NASA Ames Research Center, Moffett Field, California 94035
Corresponding author: e-mail seongsin@eng.ua.edu

Abstract— We report the growth and characterization of a new dilute nitride, InNSb quantum dots embedded on both InAs and GaAs substrate. Strain induced, self-assembled quantum dots are grown using solid-source molecular beam epitaxy. For improved growth control, we developed a growth technique similar to atomic layer epitaxial methods. Nitrogen incorporation during formation of quantum dots changes surface energy barrier and causes anisotropic distribution of strain energy, results in formation of closely coupled multiple quantum dots in <110> orientation. We obtained mid infrared luminescence around 3.6 μm from InNSb QDs grown on InAs substrate, where it exhibits relatively low efficiencies of nitrogen incorporation compared to the quantum well structure. The band structure calculation confirms band-anticrossing occurs with localized nitrogen energy band, $E_N = 0.42$ eV, and results in energy band gap reduction of 50 meV with adding 1% of nitrogen.

Keywords—quantum dots; mid-IR; self assembly; MBE;

I. INTRODUCTION

Nanophotonics plays a major role in the development of smart sensors, which require integrated functionality in detecting various chemical and biological agents, simultaneous identification, and real time information transfer. Most bi-molecules and biological agents based on proteins have strong absorption and resonance fingerprints between the mid- and far-infrared wavelength range of 3 μm and 15 μm . Therefore highly efficient, and inexpensive infrared (IR) sources and detectors are essential to the smart sensor systems. Quantum dots lasers, which have been in development for decades, have several important advantages [1-3]: (i) low power consumption due to low threshold current operation, (ii) array operation and integration due to low voltage and low current operation, (iii) large wavelength tuning due to broad gain spectrum, (iv) low cost due to simple growth and fabrication techniques. However, there has been a lack of development of IR quantum dots lasers, mainly due to the limited material systems which can fulfill the condition of operating within IR spectrum.

Recent, newly-developed III-V dilute nitride materials have interesting physical properties which may be beneficial to enable MIR and FIR devices. [4,5] The addition of small amounts of nitrogen to III-V semiconductors dramatically increases the wavelength due to the unique band interactions between nitrogen and its host material. Incorporating nitrogen

into narrow-gap materials is very attractive because it can reduce the energy gap and enable emission beyond the FIR, [6] a feat not possible with conventional III-V semiconductors. In addition, nitrogen in these materials will increase the electron effective mass, suppressing a Auger recombination. We report here the detailed growth mechanisms and characterization of a new dilute nitride narrow gap semiconductor, in which nitrogen is incorporated into an antimony based matrix: In(As)Sb. InNSb self-assembled quantum dots were successfully grown on InAs by solid source molecular beam epitaxy (MBE). The growth conditions were optimized for the formation of QDs in various conditions. The understanding and verifying the nitrogen incorporation in quantum dots is currently limited through our experiments. The optical properties of QDs were investigated through temperature and excitation power dependent photoluminescence. The detailed band structure was calculated using 8-band $k \cdot p$ method with a localized nitrogen level to verify the BAC model in narrow gap semiconductor. [6] We obtained mid-infrared luminescence emission at 3.6 μm from InNSb QDs grown on InAs substrate, which confirms the great potential of narrow gap semiconductors that incorporate nitrogen for MIR devices.

II. MATERIAL GROWTH AND CHARACTERIZATION

The InNSb strain induced self-organized quantum dots investigated in this study were grown on undoped (100) InAs substrates by solid-source molecular beam epitaxy (MBE) in a Varian Mod. Gen-II system. Indium was supplied by a SUMO effusion cell. A valved arsenic cracker supplied As_2 and an unvalved antimony cracker supplied monomeric antimony (Sb). Nitrogen was supplied by a modified SVT Associates plasma cell operating at a radio frequency (rf) of 13.56 MHz. Nitrogen gas with 5N (99.999%) purity was filtered through a <1 part-per-billion Pall Mini-Gaskleen purifier to minimize the presence of oxygen. The plasma cell was operated with 300 W input power and a nitrogen gas flow of 0.25 sccm. The InAs buffer layer was grown at 515°C before depositing QDs to provide a smooth InAs surface. The single layer of InNSb QDs was grown on the InAs buffer layer without capping for atomic force microscopy (AFM) measurement. For the photoluminescence measurement, a single and double QDs

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 2008		2. REPORT TYPE		3. DATES COVERED 00-00-2008 to 00-00-2008	
4. TITLE AND SUBTITLE Optical Properties of Closely Coupled Dilute Nitride Mid-Infrared InNSb Quantum Dots				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Electrical and Computer Engineering, The University of Alabama, Tuscaloosa, AL, 35487				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002137. Proceedings of the 2008 IEEE International Conference on Nanotechnology (8th) Held in Arlington, TX on August 18-21, 2008. U.S. Government or Federal Rights License					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

layers were grown with same growth conditions of AFM sample, but with an InAs capping layer on top of the InNSb QDs. [7]

To grow QDs, the growth temperature was reduced to 390°C, as measured by pyrometry. The indium growth rate was 0.086–0.10 monolayer (ML)/s determined using beam equivalent pressure (BEP) measurements. Reflection high-energy electron diffraction (RHEED) patterns were observed during growth to study the growth surface before and after QD formation. The substrate was rotated with 12 rpm. Photoluminescence (PL) measurements at various temperatures and excitation powers were performed with the sample mounted on a cold finger in a cryostat and cooled by liquid helium down to 10K. The sample was excited by a 630nm high power diode laser with a maximum pumping density of 1W/cm² attenuated using neutral density filters. The PL signal was collected through a monochromator by a liquid nitrogen cooled InSb detector that has a cutoff wavelength of 4.8 μm, in a standard synchronous detection scheme.

III. RESULTS AND DISCUSSION

Figure 1 shows the formation of InSbN quantum dots as observed by *in-situ* RHEED. According to our *in-situ* RHEED studies, the transition of planar growth (2D) to island growth (3D) was occurred at around 2.2 ML which was compared with InSb QD formation, which observed the transition from 2D to 3D at around 1.2 ML growth thickness. (not shown) This can be used as an indirect evidence of nitrogen incorporation in InNSb quantum dots where the lattice mismatch decreased as a small amount of nitrogen incorporated resulted in thicker 2D layers before accumulated strain was relieved through 3D structure. The actual amount of nitrogen incorporation is hard to measure directly at this time and will be further investigated. Another interesting surface feature from the RHEED was what the 2D growth looks like before the QDs are formed. The bright and clear 2x4 diffraction pattern indicates the very smooth 2D layer can be deposited with a high strain between InSbN and InAs.

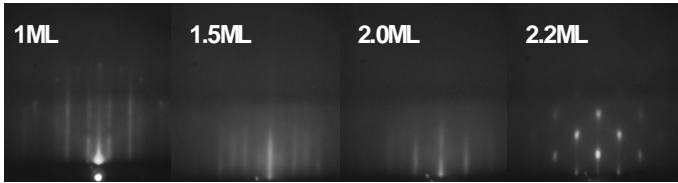


Figure 1 Series of *in-situ* RHEED pattern observation of transition from 2D to 3D of InNSb QDs at 2.2 ML.

Figure 2 shows AFM images of two samples with different thickness of deposition of InNSb quantum dots. The left image is the 2.2 ML thick growth of InNSb quantum dots obtained immediately before the transition from 2D to 3D growth, as we clearly observed in the RHEED pattern. The dots density is about $8 \times 10^{10} \text{ cm}^{-2}$. The right image is the 4ML deposition of InNSb quantum dots where dots were laterally coupled to one another. The dots density is about $3 \times 10^9 \text{ cm}^{-2}$. The section analysis of the AFM images confirmed that the double dots are

regular shaped small dots coalesced together as shown in the right image. The double QD images are not due to AFM-tip artifacts and are independent of the AFM tip and sample orientation during measurement. Furthermore, SEM measurements confirm the formation of double QDs in the samples. Since the growth rate was slower than the substrate rotation rate, we also can exclude the shadowing effects of the molecular beam, and the formation of the coupled dots is more likely due to the surface's atomic configuration.

AFM measurements rather show a dynamic change in the QD formation from the beginning and a dependence on layer thickness, which is also strongly related nitrogen exposure time during the ripening process of QDs. The nitrogen incorporation process may change the surface energy barrier during formation of quantum dots and causes anisotropic distribution of strain energy, resulting in the formation of coupled multiple quantum dots. [8] We observed the dots were regularly distributed in $\langle 110 \rangle$ orientation and 98% QDs formed in this growth condition were laterally coupled QDs.

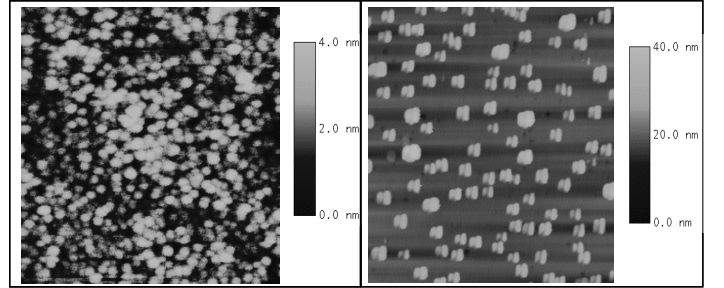


Figure 2 AFM images of (a) 2.2 ML growth thickness of InNSb QDs, (b) 4ML growth thickness

To explore the origins of multiple QD nucleation, we focus on the growth mechanisms governing the deposition and the hopping process of atoms on the surface at low growth rate [9]. The probability of an atom hopping from one lattice position to another is given by the Arrhenius factor,

$$r = v \exp(-E/k_B T)$$

where v is the frequency of attempt, E is the hopping barrier, k_B is Boltzmann's constant, and T is the growth temperature. In the Stranski-Krastanow growth mode, the hopping barrier is given by $E = -E_s + nE_b + E_{str}$. E_s is the surface binding energy of an adatom to the wetting layer, E_b is the bond energy to the nearest neighbor's atom, n is the number of the nearest neighbor atoms, and E_{str} is the energy due to the generated strain field in the vicinity of QDs which have already nucleated [10]. The strain energy distribution around and within the QDs is anisotropic, with minima on the boundaries of the QDs. The hopping barrier is therefore lower for the atoms located on the boundary of QDs, leading to a higher hopping rate. In our model, a low growth rate allows for sufficient chemical reaction time and the adatoms can move from the boundary of the existing QDs to the next lattice

position, forming a new QD close to the existing one. The formation of multiple QDs occurs.

Figure 3 shows the QDs size changes as increasing the growth thickness for both InNSb QDs and InSb QDs. The relation is somewhat different as the nitrogen is introduced and it is consistent with the occurrence of the ripening process in InNSb QDs. The ripening process and the coalescence of two single dots limit the QDs size, even though the growth thickness increases, and the changes of QDs size were comparably smaller than the changes in InSb QDs.

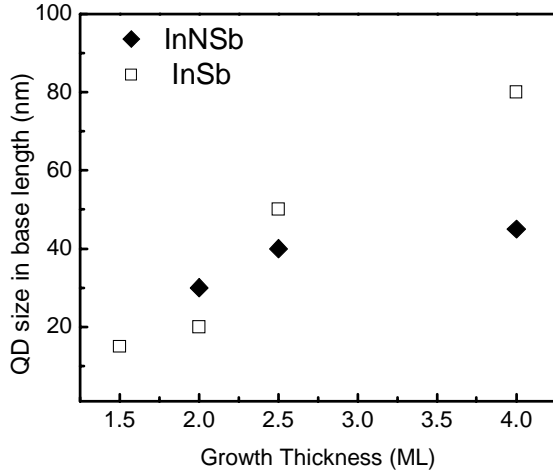
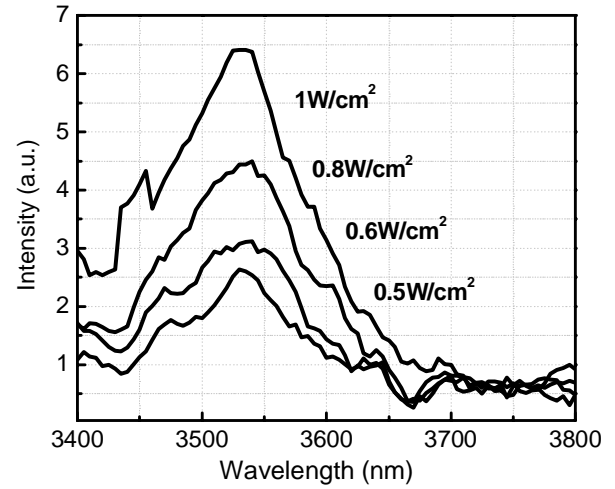


Figure 3 QD size dependence on growth thickness for both InNSb and InSb QD

Figure 4 shows the 10K photoluminescence spectra from closely coupled InNSb double QDs under different excitation powers. The ground peak emission has been obtained at around 3.55 μm and it is the first reported MIR luminescence from dilute nitride Sb based quantum dots grown by MBE. At very low excitation power, the clear resolution of an excited state was observed, and the peak position didn't change as increasing the excitation powers. This behaviour can be compared with the photoluminescence characteristics obtained from the most dilute nitride based materials in 2D structure, where it showed the blue shift of peak position with increasing the excitation powers. It is widely accepted that the luminescence indeed comes from the nitrogen related localized states. Localized emission typically exhibits a blueshift of the peak PL wavelength with increasing excitation density because an increase of the excitation density fills the energy states in the band tails. [7,11,12] However, QDs usually has limited in

thermal process, since the density of states are discrete,



therefore such a blueshift can't easily occur, where we observed the peak position is rather unchangeable in this QDs. In addition, the process of nitrogen incorporation in QDs is more dynamic than simply forming the localized states. The nitrogen introduced may contribute in many different ways such as a change of the surface energy boundaries before forming the QDs, and incorporation is limited in such a small volume of QDs that might prevent from the formation of localizing states induced by nitrogen.

Figure 4 10K Photoluminescence spectra of closely coupled InNSb QDs under different excitation powers.

Figure 5 shows the temperature dependent PL measurement results. We obtained PL signals with reasonable intensities up to 120K. The PL peak energy of the InNSb QDs changed in the negligible amount and integrated PL intensity varied with increasing temperature. PL intensities decrease with increasing temperature between 10K and 80K that satisfy the equation of a thermal quenching between the integrated PL intensities and temperature,

$$I_{PL} = I_0 / [1 + A \cdot \exp(T / T_0)], \quad (1)$$

where I_{PL} is the integrated PL intensity, T is the measured temperature, T_0 is a characteristic temperature, A is a tunneling factor, and I_0 is the integrated intensity at the low temperature limit. From the equation, we obtain characteristic temperature T_0 that is approximately 100K.

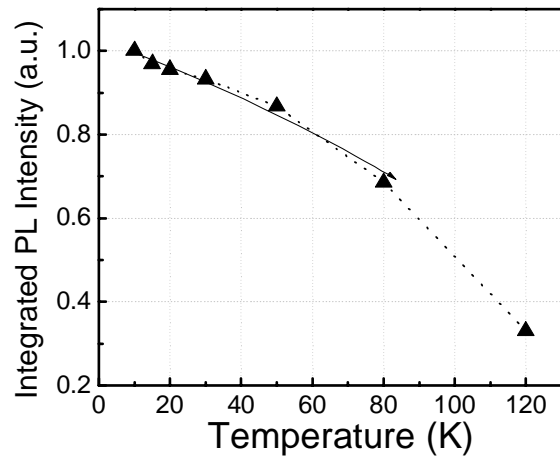


Figure 5 Temperature dependent integrated PL intensity of InNSb closely coupled QDs

The very strong argument of PL intensity drop at 80K comes from the band offset and band alignment between InNSb and InAs capping layer. Based on our calculation, where the conduction band interaction with a localized nitrogen band at $E_N=0.42$ eV, the conduction band reduction of InNSb would be only 50meV, which results the expected band alignment belongs to the type-II structure. [13,14] The strong carrier spill over seems to occur as elevating the temperature since the current structure didn't have properly designed barrier layers.

IV. CONCLUSION

In summary, we investigated the growth and optical properties of self-assembled InNSb QDs grown on GaAs substrate by Molecular Beam Epitaxy. We studied the impact of several growth parameters and techniques on the formation of QDs. Our results show a strong tendency of forming InNSb laterally coupled QDs, which may be explained by the very low bond energy of InSb and the anisotropic distribution of strain energy within QDs. Temperature dependent and power dependent PL measurements obtained and first report the MIR emission at $3.55\ \mu\text{m}$ from InNSb QDs grown on InAs substrate.

By utilizing the unique behaviour of dilute nitride III-V semiconductors, these results provide great promise to extend conventional narrow gap materials to the MIR and FIR wavelengths required for biosensing devices.

REFERENCES

- [1] P. Caroff, C. Paranthoen, C. Platz, O. Dehaese, H. Folliot, N. Bertru, C. Labbe, R. Piron, E. Homeyer, A. Le Corre, and S. Loualiche, *Appl. Phys. Lett.* **87**, 243107 (2005).
- [2] N. Yamamoto, K. Akahane, S. Gozu, and N. Ohtani, *Appl. Phys. Lett.* **86**, 203118 (2005).
- [3] S. M. Kim, Y. Wang, M. Keever, and J.S. Harris, *IEEE Photonics Tech. Lett.* **16**, 377 (2004)
- [4] *Dilute Nitride Semiconductors*, Ed. Mohammed Henini, Amsterdam: Elsevier, pp. 1-92, January 2005, and references within.
- [5] W. Shan, W. Walukiewicz, J. W. Ager, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.*, **82**, 1221 (1999).
- [6] S.M. Kim, H. B. Yuen, F. Hatami, A. Chin, J. S. Harris, MRS Fall meeting, Boston (2006)
- [7] H.B. Yuen, S.M. Kim, F. Hatami, and J.S. Harris, *Appl. Phys. Lett.* **89**, 121921 (2006)
- [8] M. Zinke-Allmang, L.C. Feldman, and M.H. Grabow, *Surf. Sci. Rep.* **16**, 377 (1992).
- [9] M. Meixner, E. Schöll, M. Schmidbauer, H. Raidt, and R. Köhler, *Phys. Rev. B* **64**, 245307 (2001).
- [10] P.Möck, G.R. Booker, N.J. Mason, R.J. Nicholas, E. Aphandery, T. Topuria, N.D. Browning, *Material science and engineering* **B80**, pp. 112-115 (2001).
- [11] I. A. Buyanova, W. M. Chen, G. Pozina, J. P. Bergman, B. Monemar, H. P. Xin and C. W. Tu, *Appl. Phys. Lett.*, **75**, 501 (1999).
- [12] L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, C. Vannuffel, A. Million, and A. Chenevas-Paule, *Appl. Phys. Lett.*, **76**, 2241 (2000).
- [13] W. Shan, W. Walukiewicz, J. W. Ager, E.E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.*, **82**, 1221 (1999); J. Wu, W. Shan, and W. Walukiewicz, *Semicond. Sci. Technol.*, **17**, 860 (2002)
- [14] B. N. Murdin, A. R. Adams, P. Murzyn, C. R. Pidgeon, I. V. Bradley, J.-P. R. Wells, Y. H. Matsuda, N. Miura, T. Burke and A. D. Johnson, *Appl. Phys. Lett.*, **81**, 256 (2002).